

## METHOD FOR INCORPORATING ADDITIVES IN AN OPHTHALMIC ARTICLE BY MEANS OF A SUPERCRITICAL FLUID

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### BACKGROUND OF THE INVENTION

The present invention relates generally to a method for incorporating additives in an ophthalmic article made of organic glass by means of a fluid in the supercritical state.

10 The present invention more particularly relates to a method for incorporating additives, such as stabilizers, antioxidants, antiozonants, UV absorbers, plasticizers, dyes and pigments (photochromic substances and conventional dyes and pigments), in finished or semi-finished ophthalmic articles made of transparent organic polymers by means of a supercritical fluid for example CO<sub>2</sub> in the supercritical state.

15 There exists a number of conventional methods for incorporating an additive, in particular a photochromic substance, in a substrate made of transparent organic polymers of an ophthalmic article.

A first conventional method consists in incorporating the various additives in the transparent and liquid monomer composition, in pouring the liquid monomer composition in which the additives are incorporated  
20 between the two parts of a mold and in then polymerizing the monomers in order to obtain the ophthalmic article comprising a substrate made of organic glass in which the desired additives are found enclosed. This technique exhibits a number of disadvantages. In particular, when the  
25 additives are photochromic pigments or UV absorbers, this method requires polymerization by the thermal route, since the presence of the UV absorber and/or of the photochromic pigments does not generally make possible, or only with great difficulty, a photochemical polymerization. Moreover, the incorporation of photochromic compounds in the case of the use of allylic  
30 monomers is virtually ruled out, the method requiring the use of a high concentration of initiator, long polymerization time and relatively high polymerization temperatures. When the additive incorporated is a photochromic substance, there is a risk that the long polymerization times and the relatively high polymerization temperatures will cause degradation  
35 of the photochromic substance.

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Moreover, it is not ruled out that degradation of the photochromic substance is generated by reaction of the latter with radicals originating from thermal or photochemical initiators.

Another conventional technique, used to incorporate conventional dyes in an ophthalmic article, consists in immersing the ophthalmic article, composed of a transparent polymer substrate, in an aqueous dispersion of insoluble dye particles and in heating at a temperature of the order of 90°C for a time sufficient to cause the dye particles to penetrate into the surface of the polymer substrate. This technique also exhibits a number of disadvantages. First of all, the dispersion has a limited lifetime and has to be discarded after a relatively short time, resulting in a significant loss of dye or requiring expensive stages for recovering the dye. This method is not applied to all types of substrates or polymers and requires, for substrates which are the most resistant to dyeing, the use of an aggressive vector agent (for example phenol derivatives), which results in problems of discharges and risks of environmental pollution. Finally, the incorporation of the dye remains superficial, that is to say that the dye does not penetrate very far under the surface of the substrate, which does not make possible a core dyeing of the substrate.

A recently developed technique, more particularly for the introduction of a photochromic substance into ophthalmic articles comprising a transparent polymer substrate, is the so-called "thermal transfer" technique. This thermal transfer method is described, inter alia, in the documents US 4.286.957 and 4.880.667. In this technique, a surface of the transparent polymer substrate is coated with a layer of a varnish containing the photochromic substance to be incorporated. The substrate, thus coated, is then treated thermally in order to cause the photochromic substance to migrate into the substrate. This method also exhibits a number of disadvantages. The heating time necessary to cause the photochromic substance to migrate is relatively long, of the order of 5 hours. Only part of the photochromic substance is introduced into the substrate, so that there are not insignificant losses of photochromic substance. Finally, this method only makes possible a low depth of penetration of the photochromic substance into the substrate, of the order of 150  $\mu\text{m}$  at most.

In the case of the incorporation of a photochromic substance, it is desirable to obtain the greatest possible penetration of this substance into the substrate. This is because the deep layers of photochromic substance act as a reservoir. Thus, as the surface layers of photochromic substance lose, under the effect of repeated UV irradiations, their photochromic characteristics, they are replaced by intact underlying layers of photochromic substance, which prolongs the lifetime of the photochromic ophthalmic article.

The document US-A-4.598.086 describes a method for impregnating a thermoplastic polymer with an impregnation material (namely a fragrance, a disinfecting or rat-killing agent or a pharmaceutical composition) by dissolving the impregnation material in a volatile blowing agent (for example, CO<sub>2</sub> maintained at or near supercritical conditions), causing the thermoplastic polymer to swell by bringing it into contact with the volatile blowing agent in the supercritical state or near supercritical state containing the impregnation material, and by reducing the pressure, so that the volatile blowing agent diffuses from the polymer.

The polymers act solely as support for an active product which must subsequently be released in a controlled way.

The document US-A-4.820.752 describes a method for infusing an additive into a polymer by dissolving the additive in a gaseous fluid solvent (for example CO<sub>2</sub>) which has a boiling point below room temperature and a density of at least 0.01 g/cm<sup>3</sup>, by bringing the solution of the additive and the fluid solvent into contact with a polymeric material for a time sufficient to enable at least part of the solution to be absorbed into the polymeric material, and by separating the fluid solvent from the polymeric material, leaving the infused additive therein.

Although this document envisages the use of a supercritical fluid, this condition does not appear to be essential for the method described. Moreover, the only example using a fluid in the supercritical state relates to the incorporation of progesterone in a polyurethane substrate.

The document US-A-5.340.614 describes the impregnation in a polymer substrate of additives which are insoluble in a supercritical fluid which consists in bringing the polymer substrate, the impregnation additive

and a liquid vehicle, such as water, into contact simultaneously in the presence of a supercritical fluid.

The document WO 95/20476 describes the treatment of ophthalmic lenses with a fluid in the supercritical state in order to remove incompletely  
5 polymerized materials therefrom.

### SUMMARY OF THE INVENTION

It would thus be desirable to have available a method for incorporating photochromic additives in finished and semi-finished  
10 ophthalmic articles comprising a transparent polymer substrate containing at least one free plasticizer which can be applied to all types of polymers which can be used for the manufacture of photochromic ophthalmic articles, which makes it possible to adjust at will the depth of penetration of the photochromic additives into the substrate and which in particular makes  
15 possible a core penetration of the additives, even into relatively thick substrates. In addition, this method should make possible short treatment times, should not degrade the photochromic properties of the incorporated additive, should not degrade the physical and optical properties nor the geometry of the polymer substrate of the ophthalmic article, and should not  
20 elute the additives already present in the substrate, and in particular the free plasticizer.

By free plasticizer, it is meant a plasticizer that does not have chemical linkages with the polymer network constituting the substrate.

Thus, the method must not harm in particular the geometry of the  
25 polymer substrate, that is to say that it must not deform the polymer substrate to a point such that it will be necessary to reshape the ophthalmic article after the incorporation of the additive. In addition, the method must not harm the advantageous properties of the ophthalmic article, such as the resistance to scratching and to abrasion and the impact strength.

30 In addition, this method must make possible a homogeneous incorporation of the additive within the polymer substrate. The additive introduced must not be subject to a release phenomenon. Finally, the method must not detrimentally affect the resistance to ageing of the ophthalmic article.

According to the invention, a method for incorporating at least one photochromic additive in a finished or semi-finished ophthalmic article comprising a transparent polymer substrate containing at least one free plasticizer which comprises :

- 5       - introducing a supercritical fluid into a reactor containing the ophthalmic article and the photochromic additive to be incorporated ;
- maintaining the supercritical fluid in the reactor, in a static state, for a predetermined period of time, in order to obtain the incorporation of the photochromic additive in the polymer substrate of the ophthalmic article to
- 10     a predetermined depth ;
- removing the supercritical fluid ; and
- recovering the ophthalmic article in which the photochromic additive has been incorporated.

A specific implementation of the method according to the invention  
15 relates to a method for the photochromization of a finished or semi-finished ophthalmic article comprising a transparent polymer substrate which comprises :

- A. A first stage comprising :
  - the insertion into a reactor of a transparent polymer substrate and
  - 20     of a plasticizer for the substrate,
  - the introduction into the reactor of a supercritical fluid,
  - the maintenance of the supercritical fluid in the reactor, in a static state, for a predetermined period of time, in order to obtain the incorporation of the plasticizer in the polymer substrate, and
  - 25     • the removal of the supercritical fluid ; and
- B. A second stage comprising :
  - the insertion into the reactor containing the plasticized polymer substrate of one or more photochromic compounds ;
  - the introduction of a supercritical fluid,
  - 30     • the maintenance of the supercritical fluid in the reactor, in a static state, for a predetermined period of time, in order to obtain the incorporation of the photochromic compound or compounds in the plasticized polymer substrate of the ophthalmic article to a predetermined depth,
  - 35     • the removal of the supercritical fluid, and

- the recovery of the ophthalmic article in which the photochromic compound or compounds are incorporated.

### BRIEF DESCRIPTION OF THE DRAWINGS

5 Fig. 1 shows a representative device that may be used in the practice of this invention.

Fig. 2 shows a representative reactor that may be used in the practice of this invention;

Fig. 3 and Fig. 4 show graphs of the data from examples 1-3.

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### DETAILED DESCRIPTION OF THE INVENTION

Materials are generally known in three states : solid, liquid and gaseous. Materials change from one to another of these states when the temperature and/or the pressure is/are varied. Now, there exists a point  
15 beyond which it is possible to change from the liquid state to the gaseous or vapor state without boiling or, conversely, without condensing, thus without changing : this point is known as the critical point.

A fluid in a state characterized either by a pressure and a temperature which are respectively higher than the critical pressure and the critical  
20 temperature, in the case of a pure body, or by a representative point (pressure, temperature) situated beyond the boundary of the critical points represented on a diagram (pressure, temperature), in the case of a mixture, is said to be in the supercritical state.

Carbon dioxide proves to be a particularly advantageous fluid for  
25 being used as fluid in the supercritical state, because of its critical parameters ( $t_c = 31^\circ\text{C}$ ,  $P_c = 7.3 \text{ MPa}$ ), its absence of toxicity, its non-polluting nature and its low costs.

The use of  $\text{CO}_2$  in the supercritical state as fluid in the supercritical state is thus recommended in the method according to the invention. The  
30 ophthalmic articles which can be treated by the method of the invention are finished or semi-finished articles comprising a transparent polymer substrate.

The finished ophthalmic articles are ophthalmic articles obtained in their definitive shape, generally by pouring polymerizable compositions  
35 between two molds exhibiting required surface geometries and then

polymerizing. An article is then obtained, the two faces of which are in their final state.

It is often the case that semi-finished articles are manufactured which comprise, after molding, a single face with its final geometry, it being possible for the second face then to be surface-finished as required.

The ophthalmic articles according to the invention comprise, for example, spectacle lenses, sun or corrective lenses, hard or soft contact lenses and hydrogel contact lenses in the dry state.

The ophthalmic articles can also, before the treatment by the method of the invention, contain layers of abrasion-resistant varnish and layers for increasing the impact strength on one of the surface of the transparent polymer substrate.

The polymers of the transparent substrate of the ophthalmic articles which can be used in the method of the invention are all transparent polymers, copolymers and mixtures of the latter which are suitable for the formation of ophthalmic articles.

Mention may be made, among the polymers and copolymers which can be used in the present invention, of allylic polymers, polyol (allyl carbonate) polymers, polyacrylates, poly(alkyl acrylate)s, such as poly(methylmethacrylate)s or such as poly(ethoxy)biphenol A di(meth)acrylates, polyurethanes, polythiourethanes and polycarbonates.

The particularly recommended polymers and copolymers are polycarbonates, such as poly(4,4'-dioxycyclohexyl-2,2-propane carbonate), poly(ethoxy)biphenol A dimethacrylate, polyethylene glycol dimethacrylate (PEG dimethacrylate), poly(methyl methacrylate) or poly(allyl carbonate)s, such as diethylene glycol bis(allyl carbonate) and its copolymers.

The polymers and copolymers used for the manufacture of ophthalmic articles are well known and are described, inter alia, in the documents WO 95/10790 and EP-A1-0.653.428.

Besides photochromic substances and plasticizers, the additives which can be incorporated in the polymer substrate of the ophthalmic articles by means of the method according to the invention comprise all additives generally used in polymer substrates of ophthalmic articles and in particular UV absorbers, infrared absorbers, materials for laser screens,

stabilizers, antioxidants, conventional dyes and pigments, anti-odor agents, perfumes and mixtures thereof.

The additives which are particularly recommended with the process of the present invention are dyes and pigments and very especially  
5 photochromic substances.

Mention may be made, among the UV absorbers which can be used in the present invention, of benzophenones, dihydroxybenzophenones or benzotriazoles. Use may be made, among the stabilizing agents, of sterically-hindered amines.

10 Mention may be made, among the materials for laser screens, of porphyrin complexes, phthalocyanine derivatives and their mixtures. Such materials are described in the document US-A-4.657.345.

Mention may be made, among the antioxidants which can be used in the present invention, of phenolic antioxidants, such as monophenols,  
15 bisphenols and thiobisphenols, phosphites, such as 4,6-di-tert-butylphenyl phosphite and triphenyl phosphite, or phosphines, such as triphenylphosphine.

Mention may be made, among the plasticizers which can be used in the present invention, of linear or branched phthalates, such as the  
20 phthalates of C<sub>6</sub>-C<sub>12</sub> alcohols, in particular dioctyl phthalate (DOP), and isophthalates, such as diisodecyl phthalate (DIOP), diisononyl phthalate (DINP) and diisooctyl phthalate (DIOP), as well as benzyl butyl phthalate (BBP) and diisoundecyl phthalate (DIUP), or C<sub>18</sub>-C<sub>30</sub> fatty acid esters, such as adipates, sebacates and azelates.

25 A preferred class of plasticizers is poly(ethylene glycol)dibenzoates.

Use may be made, among the conventional dyes and pigments, of all dyes and pigments which are conventional in coloring ophthalmic articles, such as, in particular, azo and anthraquinone pigments. Use is preferably made of lipophilic pigments.

30 Dyes which are particularly useful in the method of the present invention are photochromic substances. These photochromic substances are well known in the art and are substances which, when they are irradiated by a light beam of appropriate wavelengths, change color and return to their original color as soon as the irradiation ceases. Mention may be made,  
35 among the photochromic substances which can be used, of benzopyran



(chromene) derivatives, in particular naphthopyrans and preferentially diaryl[2H]naphthopyrans, and spirooxazine derivatives. Chromene derivatives are well known in the art and are described, inter alia, in United States Patent N°US-3.567.605, International Applications N°90/07507 and  
5 N°91/00861 and European Patent Applications EP-0.246.114 and EP-0.401.958..

Spirooxazine derivatives are also well known and are described, inter alia, in numerous patents and patent applications, such as United States Patents US 5.139.707 and US 5.114.621 (R. Guglielmetti and P. Tardieu)  
10 and European Patent Application EP-0.245.020.

Very clearly, the additives incorporated in the ophthalmic articles by the method of the present invention must not harm the optical properties of the articles obtained.

As indicated above, an important characteristic of the method of the  
15 invention is that the additive is brought into contact with the ophthalmic articles in a reactor in the static state in the presence of a fluid in the supercritical state.

Use may be made of any fluid in the supercritical state which is inert with respect to materials constituting the polymer substrate of the  
20 ophthalmic article and additive or additives to be introduced. Mention may be made, among the fluids which can be used according to the invention, of CO<sub>2</sub>, NO<sub>2</sub>, ethylene, ethane and chlorotrifluoromethane.

As indicated above, a particularly recommended fluid is carbon dioxide (CO<sub>2</sub>) because it is nontoxic and inexpensive and it can be easily  
25 recycled.

The temperature and pressure conditions of the fluid in the supercritical state will very clearly depend on the critical point of the fluid and on the nature of the polymers of the substrate and of the additives to be incorporated. However, it is recommended that the temperature of the fluid  
30 in the supercritical state should be lower by 30°C or more, preferably lower by 50°C, than the glass transition temperature (T<sub>g</sub>), under normal conditions, of the polymer polymers of the substrate of the ophthalmic article treated.

The duration of the treatment will very clearly depend on the  
35 temperature and pressure conditions of the fluid in the supercritical state, on

the nature of the polymer substrate and of the additive to be incorporated, and on the amount and on the depth desired for the incorporation of the additive. In general, it has been found that a duration of 1 to 30 minutes, preferably of 5 to 20 minutes and better still of the order of 10 to 15 minutes was sufficient to obtain the desired incorporation.

Once the incorporation of the additive has been completed, the fluid in the supercritical state absorbed by the substrate is removed. This removal is carried out easily by bringing the substrate back to atmospheric pressure, thus causing expansion of the gas.

The process according to the invention has many advantages. It does not use a solvent and consequently risks of pollution are avoided and the cost related to the possible removal and the possible reprocessing of solvents are eliminated. It makes possible efficient use of the amount of additives because they can be employed until the amount of additives initially introduced into the reactor has been completely exhausted, and consequently prevents additives from being lost and wasted. This economic aspect of the method according to the invention is particularly advantageous for the incorporation of relatively expensive additives, such as photochromic substances. In addition, the method according to the invention makes it possible to adjust the amount and the depth of incorporation of the additive into the polymer substrate and, in particular, makes it possible to obtain a core incorporation, even in significantly thick substrates. Thus, it is possible to carry out incorporations of additives, in particular of photochromic substances and dyes, to depths of 10 mm, preferably of 1 to 2 mm.

By way of comparison, the thermal transfer process only makes it possible to incorporate photochromic substances to depths of the order of 150  $\mu\text{m}$ .

The method according to the invention also makes it possible to incorporate additives, in particular photochromic substances and dyes, in polymer substrates regarded until now as difficult or even impossible to color, such as polycarbonate substrates or substrates coated with an abrasion-resistant and/or impact-resistant layer.

The following examples illustrate the present invention without, however, limiting it.

The incorporation of the additives was carried out in the laboratory device represented diagrammatically in Figures 1 and 2.

The device represented in Figure 1 comprises a CO<sub>2</sub> source connected to a pump 2 which is itself connected to a high-pressure tubular reactor 3 placed in an oven 4.

Valves make it possible to isolate the CO<sub>2</sub> source from the pump 2 and the reactor 3.

As it seen in Figure 2, the reactor 3 comprises a tubular body 5, the two ends of which are closed by plates made of sintered glass 6 and 7 and stoppers 8 and 9. The stopper 8 is provided with means for introducing CO<sub>2</sub> and is connected to the pump 2. Inside the tubular body 5 of the reactor, a transparent polymer substrate 10 for an ophthalmic article is placed between two cotton pads 12, 13, while an additive 11 or a mixture of additives intended to be incorporated in the substrate is placed in the reactor, next to the substrate 10, between the cotton pad 13 and a third cotton pad 14.

When operating, CO<sub>2</sub> is introduced from the source 1 into the reactor 3 and brought to the pressure greater than the critical pressure and heated by means of the oven to a desired temperature greater than the critical temperature. The CO<sub>2</sub> is maintained under the chosen supercritical conditions, in the static state, in the reactor 3 for predetermined time necessary for the incorporation of the additive. At the end of the incorporation, the CO<sub>2</sub> is removed from the reactor and from the substrate by returning the pressure and the temperature to ambient pressure and temperature (generally normal pressure and temperature or close to normal) and by allowing the CO<sub>2</sub> to discharge from the substrate under these ambient pressure and temperature conditions. The substrate incorporating the additive is then recovered.

#### EXAMPLES 1 to 3

Three test specimens, with a thickness of 1 mm, of a polymer substrate obtained by polymerization of the following polymerizable composition, described in Patent Application WO 95/10790, were treated in the reactor described above.

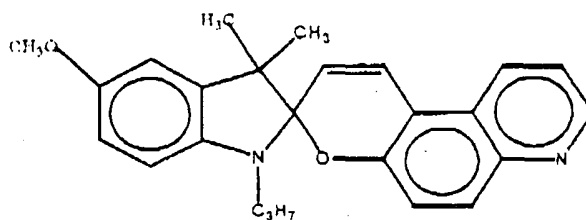
Base Ingredients	Parts by weight
Ethoxybisphenol A dimethacrylate containing 2.5 ethoxy units	43.5
Poly(ethylene glycol) with a molecular mass of 600, terminated at both ends by methacrylate	21.0
1,3-Diisopropenylbenzene	6.0
2-Phenoxyethyl methacrylate	20.5
Poly(ethylene glycol) with a molar mass of 200, containing a benzoate ending at both ends	8.7
Triphenyl phosphite	0.3
Diethyl pyrocarbonate	0.15
Initiator	
Diisopropyl peroxydicarbonate	1.5
OO-tert-Butyl O-2-ethylhexyl mono-peroxydicarbonate	0.5

- 5 The polymerizable composition is poured into a flat-sheet mold. The mold is placed in a circulating air oven and the composition is cured by using following curing cycle.

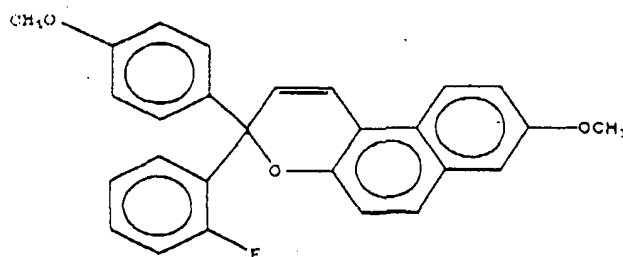
Cumulative hours	Temperature of the oven °C
0	34
24	36
32	44
34	46
36	48
38	50
40	54
42	58
44	64
46	69
48	85
49	105
49.5	130
50.5	130 (end of the cycle)

The polymerizable is allowed to cool in the oven back to approximately 80°C and is then withdrawn from the oven and removed from the mold.

The additive to be incorporated was a mixture of photochromic substances comprising 55% by weight of a compound of formula :



described in Patent Application WO 90/12819 ("blue" dye), and 45% by weight of a compound of formula :



described in Patent Application WO 90/17071 ("orange" dye).

100 mg of the above mixture was placed in the reactor.

5 The operating conditions for the supercritical CO<sub>2</sub> were as follows :

P = 20 MPa

T = 80°C

Density  $\rho_{\text{CO}_2} = 0.6 \text{ g/cm}^3$ .

Each of the test specimens of Examples 1 to 3 was subjected to a  
10 different treatment time, namely 5, 15 and 20 minutes respectively.

The test specimens obtained are virtually colored to the core.

The degree of impregnation of the photochromic substances into the  
substrate was monitored by UV spectroscopy. The results are represented in  
Figures 3 and 4, which respectively represent the absorption curves of the  
15 colorless form and of the colored form of the test specimens of Examples 1  
to 3.

The test specimens were irradiated with a Xenon lamp, 0.9 mW/cm<sup>2</sup>  
(UV), 73 klux (visible), for 15 minutes (coloring phase).

Irradiation is then stopped. A decoloring phase takes place.

20 The variation in the percentage of transmission of the test specimen  
during the two phases is measured by being placed at the wavelength  $\lambda_{\text{max}}$   
corresponding to the maximum absorption of each of the photochromic  
substances.

The kinetic study of the photochromic substances was carried out at  
25 23°C at the wavelength corresponding to the absorption maximum of each  
of the substances.

The results are shown in Tables I and II and in Figures 5 and 6.

**TABLE I**  
**("Blue" dye)**

Time in minutes	Time in seconds	% of transmission	Absorbance
0.0	0	100.1	0.000
0.2	12	74.7	0.127
0.5	30	52.8	0.277
1.0	60	37.1	0.430
1.2	72	33.9	0.470
1.4	84	31.5	0.502
1.6	96	29.8	0.525
1.8	108	28.5	0.545
2.0	120	27.5	0.560
5.0	300	22.1	0.657
10.0	600	20.2	0.694
15.0	900	19.5	0.709
15.5	930	31.2	0.505
16.0	960	41.9	0.377
17.0	1020	57.9	0.237
17.5	1050	63.4	0.198
18.0	1080	67.8	0.169
19.5	1170	76.1	0.118
20.0	1200	77.9	0.108
20.5	1230	79.5	0.100
21.0	1260	80.8	0.093
21.5	1290	81.9	0.87
22.0	1320	82.9	0.081
22.5	1350	83.7	0.077
23.0	1380	84.6	0.073
23.5	1410	85.2	0.070
24.0	1440	85.8	0.066
24.5	1470	86.4	0.063
25.0	1500	86.9	0.061
30.0	1800	90.3	0.043
35.0	2100	92.5	0.034
Coloration T1/2	Sec.	45.2	
Decoloration T1/2	Sec.	69.9	

5 measurement at 23°C, 0.9 mW/cm<sup>2</sup>, 73 klux at  $\lambda = 620$  nm.

TABLE II  
("Orange" dye)

Time in minutes	Time in seconds	% of transmission	Absorbance
0.0	0	100.1	-0.001
0.2	12	89.5	0.048
0.5	30	78.0	0.108
1.0	60	67.1	0.173
1.2	72	64.2	0.193
1.4	84	61.9	0.208
1.6	96	59.9	0.223
1.8	108	58.1	0.236
2.0	120	56.8	0.246
5.0	300	46.2	0.335
10.0	600	41.7	0.380
15.0	900	40.1	0.396
15.5	930	46.2	0.335
16.0	960	50.9	0.293
17.0	1020	58.4	0.234
17.5	1050	61.4	0.212
18.0	1080	64.0	0.194
19.5	1170	70.5	0.152
20.0	1200	72.1	0.142
20.5	1230	73.8	0.132
21.0	1260	75.2	0.124
21.5	1290	76.4	0.117
22.0	1320	77.7	0.110
22.5	1350	78.8	0.104
23.0	1380	79.8	0.098
23.5	1410	80.6	0.094
24.0	1440	81.4	0.089
24.5	1470	82.2	0.085
25.0	1500	82.9	0.081
30.0	1800	87.5	0.058
35.0	2100	89.7	0.047
Coloration T1/2	Sec.	76.1	
Decoloration T1/2	Sec.	173.3	

5

measurement at 23°C, 0.9 mW/cm<sup>2</sup>, 73 klux at  $\lambda = 490$  nm.

#### EXAMPLE 4

10 The same photochromic substances as in Examples 1 to 3 were incorporated in a polycarbonate substrate (thermoplastic Polycarbonate from the Company DALLOZ).



A plasticizer, dioctyl phthalate, was initially incorporated by using the same equipment as above and the following conditions :

$P = 20 \text{ MPa}$

$T = 80^\circ\text{C}$

5      Density  $\rho_{\text{CO}_2} = 0.6 \text{ g/cm}^3$

Duration : 15 minutes.

The photochromic substances are then incorporated in the same way with the following operating conditions :

$P = 20 \text{ MPa}$

10       $T = 80^\circ\text{C}$

Duration : 15 minutes.

The amount of plasticizer and of photochromic substances incorporated are determined by weighing. The same amount, approximately 1% by weight, of plasticizer and of photochromic substances was  
15 incorporated.

#### EXAMPLE 5.

The primary dyes shown below are incorporated in a substrate with a refractive index of 1.6, sold by the Company ESSILOR under the name  
20 ORMIL<sup>®</sup> (material regarded as exhibiting serious difficulties in coloring), by using the equipment described above and the following reaction conditions for the supercritical  $\text{CO}_2$  :

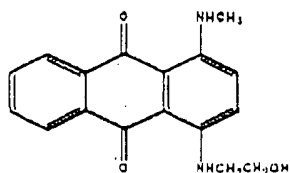
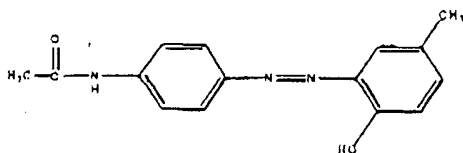
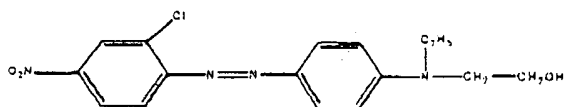
$P = 40 \text{ MPa}$

$T = 120^\circ\text{C}$

25      Density  $\rho_{\text{CO}_2} = 0.75 \text{ g/cm}^3$

The duration of treatment is 10 minutes. An intense coloring of the material is obtained.

## Structure of the primary dyes

DISPERSE BLUE  
CI 61505DISPERSE  
YELLOW 3  
CI 11855DISPERSE  
RED 13  
CI 11115

5

EXAMPLE 6

Test specimens comprising a substrate composed of the material sold by the Company ESSILOR under the name ORMA<sup>®</sup> (diethylene glycol bis(allyl carbonate) polymer), provided with an abrasion-resistant coating with a thickness of 3  $\mu\text{m}$  (varnish described in Example 3 of the document EP-A-0.614.957), a coating which is virtually impossible to color, are subjected to a treatment for incorporation of the dye "Disperse Red 13", as in the preceding examples, with the following conditions for the supercritical  $\text{CO}_2$ :

15

P = 40 MPa

T = 120°C

Density  $\rho_{\text{CO}_2} = 0.75 \text{ g/cm}^3$ 

The duration of treatment is 10 minutes. A coloring of the test specimen is obtained.

20

EXAMPLE 7

Contact lenses made of poly(methyl methacrylate) (PMMA), with a thickness of 160  $\mu\text{m}$ , were treated as described above in order to incorporate the dye "Disperse Red 13" therein. The optical parameters of the lenses, the

supercritical CO<sub>2</sub> and treatment conditions, and the results are shown in Table III below.

TABLE III

5.

Example	Optical parameters of the lens			Supercritical CO <sub>2</sub>			Duration of the treatment (min)	Coloring	Observations
	Power	Or	Diameter Ø	T (°C)	P (MPa)	$\rho$ (g/cm <sup>3</sup> )			
7	-1.75	7.70	8.50	50	8.5	0.217	10	Red transmission Tv = 90%	Undeformed appearance of a cylinder